

Mössbauer Studies of Fe-Based Ultrafine Coal Liquefaction Catalysts

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ABSTRACT:

^{57}Fe Mössbauer spectroscopy has been used to investigate a variety of ultrafine iron-based direct coal liquefaction catalysts having either Fe_2O_3 or FeOOH structure. The Mössbauer spectra of these catalysts showed pronounced superparamagnetic effects. The superparamagnetic relaxation spectra were analyzed as a function of temperature using a novel fitting model to determine the particle size distribution for these catalysts⁽¹⁾. The resulting size distributions are in the nanometer range and agree reasonably well with size information obtained by Scanning Transmission Electron Microscopy (STEM), SQUID magnetometry, and X-Ray Diffraction (XRD).

INTRODUCTION:

In recent years, there has been renewed interest in the use of iron-based catalysts for direct coal liquefaction (DCL)⁽²⁻⁷⁾. In their as-prepared form prior to liquefaction, such catalysts are normally in the form of highly dispersed iron oxides and oxyhydroxides. The Mössbauer spectra of such fine iron oxide and oxyhydroxide particles exhibit pronounced superparamagnetic relaxation effects, which have been extensively investigated⁽⁸⁻¹⁴⁾. Many of these studies of the superparamagnetic relaxation behavior of small particles have been based on an average particle volume or diameter^(8,11-14). Kundig et al.⁽⁹⁾ were the first investigators to describe a method for determining the particle-size distribution of $\alpha\text{-Fe}_2\text{O}_3$ by determining the percentage of the Mössbauer spectra in the form of magnetic hyperfine components as a function of temperature. The difficulty with this approach is that Mössbauer spectra are assumed to have sharp transitions from quadrupole doublets to magnetics on lowering the temperature. However, this transition occurs gradually, over a range temperatures. We have used a similar technique to estimate particle size distributions, with a novel model for fitting the Mössbauer spectra that incorporates a superparamagnetic component as well as magnetic hyperfine and quadrupole components.

RESULTS AND DISCUSSIONS:

When particles are small enough to behave superparamagnetically, the rapid relaxation of the particle spin system gives rise to complicated relaxation spectra which are superpositions of broadened magnetic hyperfine spectra, quadrupole doublets, and intermediate superparamagnetic (spm) spectra. Many papers have been written on the dependence of the shape of the Mössbauer spectra on the relaxation time⁽¹⁵⁻¹⁷⁾. As shown by such authors as Wickman¹⁷, the relaxation time dependent Mössbauer spectrum is given by:

$$I(\omega) = \sum_{i=1}^6 \frac{K_i [(1 + \tau \Gamma_i)P + QR]}{P^2 + Q^2} \quad (1)$$

where P, Q, R for a zero external magnetic field have the form

$$\begin{aligned} P &= \tau [\Gamma_i^2 - (\Delta - \omega)^2 + \delta_i] + \Gamma_i \\ Q &= \tau (\Delta - \omega) \\ R &= (\Delta - \omega)(1 + 2\tau \Gamma_i) \\ \delta_i &= \frac{1}{2}(\omega_{7-i} - \omega_i), \quad \Delta = \frac{1}{2}(\omega_{7-i} + \omega_i) \end{aligned} \quad (2)$$

where τ is the relaxation time in sec, ω is the frequency (in sec^{-1}) corresponding to the Doppler energy of each data point in the Mössbauer spectrum, and ω_i are the frequencies (in sec^{-1}) corresponding to the six allowed transitions between the Zeeman split energy levels. K_i are the Clebsch-Gordon coefficients with $K_6 = K_1 = 3$, $K_5 = K_2 = 2$, and $K_4 = K_3 = 1$ for zero external magnetic field. Γ_i is the natural line width in sec^{-1} and is taken to be the same for all transitions.

A novel method of fitting the spectra is developed, based on the fact that the shape of the Mössbauer spectrum changes with the relaxation time, which in turn can be related to the size of the particle⁽¹⁾. Figure 1 shows the theoretical Mössbauer spectra of $\alpha\text{-Fe}_2\text{O}_3$ at room temperature as a function of particle-size, derived from Equation 1. It can be seen that at a given temperature, particles with a diameter exceeding some critical diameter, d_M exhibit a magnetic hyperfine spectrum, while particles with a diameter less than some other critical value, d_Q , exhibit a quadrupole doublet. Particles having diameters d such that $d_Q < d < d_M$ exhibit spm relaxation spectra that are neither magnetic nor quadrupole in nature. A typical iron oxide catalyst will normally have a size distribution such that, over some range of temperature, some particles fall into all three size classifications, yielding spectra that are a mixture of magnetic, quadrupole, and spm relaxation spectra. The model consists of fitting the spectra with one or more magnetic hyperfine components corresponding to particles with $d \geq d_M$, one or more quadrupole components, representing particles with $d < d_Q$, and a single spm relaxation spectrum, representing particles for which $d_Q < d < d_M$.

To determine size distributions, the samples are run at several temperatures. The spectrum at each temperature is analyzed using the model mentioned above. The percentage of iron contributing to the magnetic hyperfine component is taken as the percentage of iron contained in particles of volume greater than the critical volume V_c at that temperature. Figure 2 shows an example of a fit obtained for a sulfated Fe_2O_3 (run at room temperature) using this model, and the size distribution obtained by running this sample at different temperatures. The concept of assigning the percentage of iron contributing to the magnetic hyperfine spectra to particles exceeding a critical volume is similar to the approach of Kundig et al⁽⁸⁾. However, the incorporation of a spm relaxation component enables the magnetic and quadrupole components to be more accurately fit, leading to a correct magnetic percentage, rather than one which artificially incorporates a substantial amount of the spm spectral absorption. A more detailed discussion of this method and its application in determining the size distributions and structures

of a variety of iron-based coal liquefaction catalysts will be published elsewhere^(1,18).

SUMMARY:

Mössbauer spectroscopy has been used to derive the size dispersion of a variety of ultrafine iron based direct coal liquefaction catalysts which show superparamagnetic behavior. A novel method of fitting the spectra was developed, in which the larger particles were represented by magnetic hyperfine components, the smaller particles by quadrupole doublets, and particles of intermediate volume by a spm relaxation spectrum. The size distributions were determined by measuring the magnetic hyperfine percentage as a function of temperature, each temperature corresponding to a critical diameter required for a magnetic Mössbauer spectrum. Comparison of the size distributions determined in this manner to size information obtained from TEM, SQUID magnetometry and XRD gave reasonable agreement⁽¹⁾. The advantage of this fitting model is that it does not assume any kind of standard distribution, but numerically fits the data itself as a combination of magnetic, quadrupole and spm component. Moreover, it is possible to obtain a rough estimate of the size distribution from a spectrum obtained at a single temperature, provided the spectrum exhibits a reasonable amount of all three spectral components (magnetic, quadrupole, and spm).

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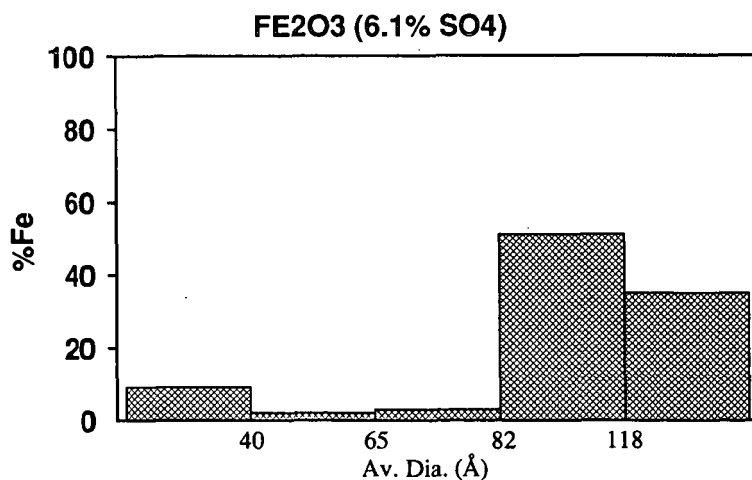
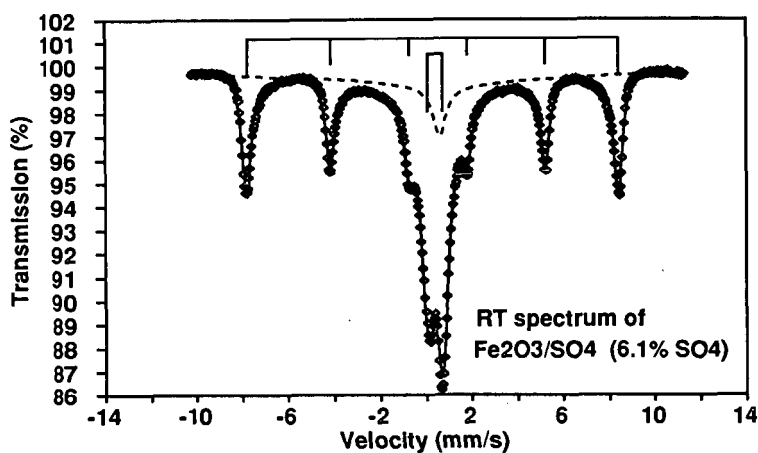


Figure 2. An example of a superparamagnetic fit and the size distribution obtained by running the sample at several temperatures.

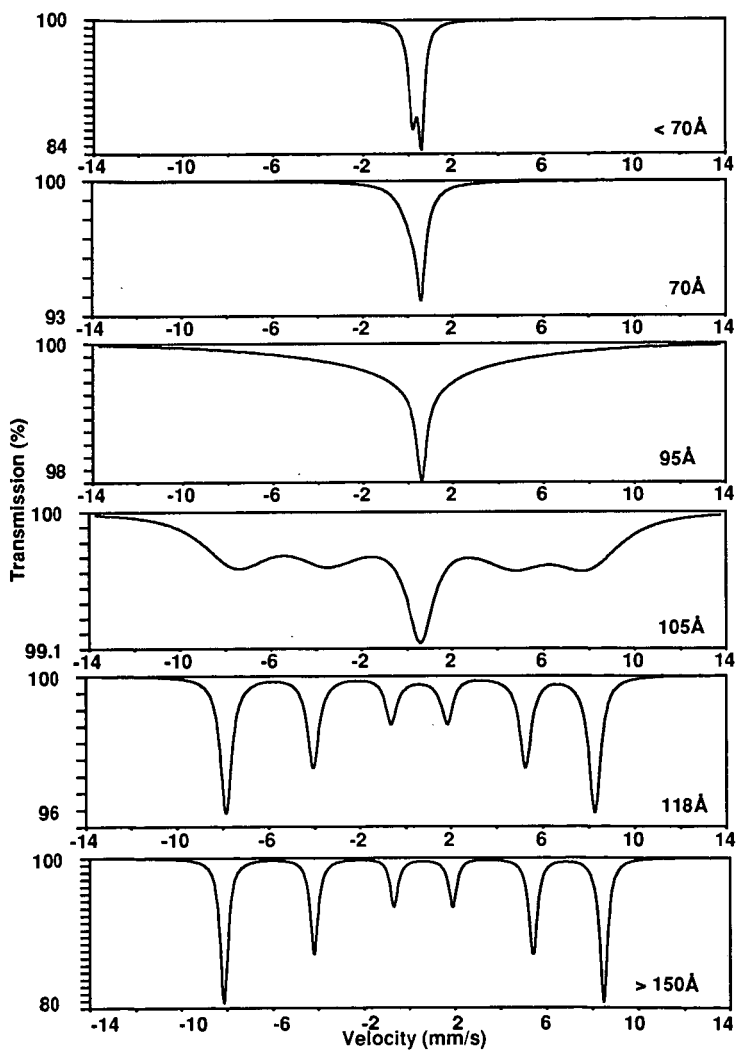


Figure 1. Theoretical plots of relaxation spectra of Fe_2O_3 at room-temperature as a function of particle size.